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Mechanism of transport of sugars across a supported liquid membrane using methyl cholate as mobile carrier

Hicham Hassoune[a,b]*, Touria Rhlalou[b], Jean-François Verchère[a]

[a]*UMR 6522 du CNRS, Université de Rouen, 76821 Mont-Saint-Aignan Cedex, France*
[b]*Université Hassan Ier, FST de Settat, B.P. 577, 26000 Settat, Morocco*

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Abstract

A supported liquid membrane was prepared by impregnation of commercial microporous polymer film with methyl cholate in cyclohexane and was used to study transport of various sugars. The stability constant and apparent diffusion coefficient of carrier-sugar complex were determined. The absence of a percolation threshold excludes a fixed-site jumping mechanism and supports a solution–diffusion mechanism of carrier–sugar complex in the membrane. However, the existence of a relation of inverse proportionality between the stability constant and the apparent diffusion coefficient suggests a mobile-site jumping mechanism where the sugar is relayed along a sequence of mobile carriers. The notable difference between the values of the stability constant of the various sugars studied confirms their molecular recognition by the methyl cholate. The $HOCH_2$ group is necessary for stable carrier–sugar complexes, this can be explained by the long distance between O-3 and O-12 of methyl cholate.

Keywords: Mechanism of transport; Supported liquid membrane; Sugars; Methyl cholate; Molecular recognition

1. Introduction

A supported liquid membranes (SLMs) may be prepared using a microporous and hydrophobic polymer of various geometries that include flat-sheet (FSSLM), hollow fiber (HFSLM) and spiral wound. The pore diameter is generally from 0.02 to 1 μm.The pores are filled with organic solvent in which the carrier is dissolved.This system offers the advantage of requiring small quantities of carrier and solvent.However, it presents a drawback of easy loss of carrier and solvent in the aqueous phases, inducing a limited lifetime of these membranes, which is the major drawback for their practical application [1–3].This loss of solvent and carrier can be explained by their solubility in the aqueous phases which are in contact

*Corresponding author.
Present address: EA 3120/LMEI, Université Paris XII, 94010 Créteil Cedex, France,
Tel. +33 (1) 45 17 14 87; Fax +33 (1) 45 17 17 21;
email: hicham.hassoune@univ-paris12.fr

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with the membrane or by formation of emulsions between the organic liquid and the aqueous phases.Consequently, the carrier and the solvent must be extremely hydrophobic.The instability of the membranes is characterized by a reduction in the permeability according to time or by a direct transport between the feed and receiving phases caused by a rupture of the system.

The development of SLMs has gained a significant importance in the separation technology, the purification in biomedical technology or in the waste water treatment [4,5]. The hollow fiber geometry is advantageous, because it allows the increase of the exchange surface.Many SLMs containing various types of carriers were described in the literature, essentially for the transport of metal ions [6–8], acids [9–11] but also for the extraction of the neutral organic molecules such as the drugs [12–14], phenol [15] and sugars [4, 5,16].

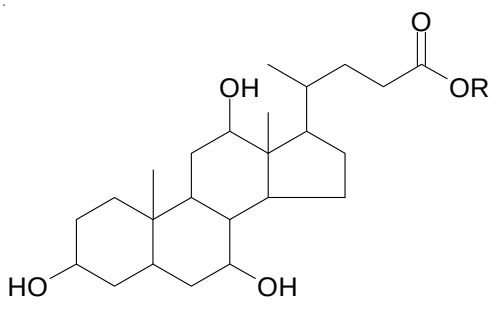
Separation by SLMs is based on the principle of the facilitated transport by specific carriers which form complexes with sugars.The boronic acids were the first carriers used and allowed a fast and selective transport of various simple sugars [17–19].The borate ion was also associated with anion-exchange membranes for facilitated transport of sugars [20,21] or to plasticized cellulose triacetate (CTA) membranes for separation of some monosaccharides (glucose and fructose) obtained by hydrolysis of sucrose [22].However, separation by boronic acids is difficult because the aqueous phases must be buffered, since these carriers form complexes only in alkaline media, in which sugars are quickly degraded.

Neutral macrocyclic carriers were already used in the SLMs [23]. Currently, the calixarenes, a family of aromatic macrocycles, require a constant interest.The calix[n]arenes (n = 4–8) are molecules in the torus formwhich can form inclusion complexes with different species such as the metal ions [24] and the amino acids [25].

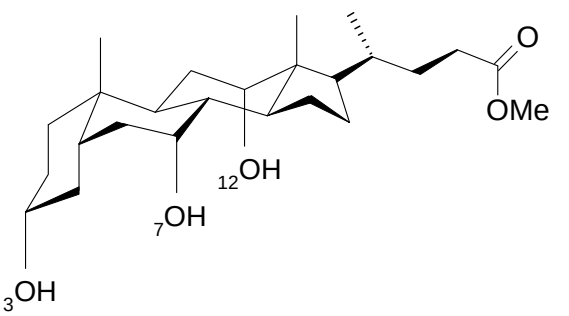
The first calixarene used was a derivative of calix[4]arene which specifically extracted several sugars in aqueous solution in tetrachloromethane [26,27].This particular type of calixarene is a resorcinarene, which is a lipophilic macrocycle obtained by condensation between the resorcinol and the dodecanal.The inventors of the resorcinarene, Aoyama and al., examined the influence of nature and the structure of sugar on the extraction [27].SLMs containing the resorcinarene were developed and used for the facilitated transport of the aldoses [28] and the alditols [29].The synthesis of the resorcinarene is difficult because this macrocycle must be obtained in specific conformation.

In previous work, we suggested another type of macrocyclic carrier which offers the advantage of being commercial [30,31].Since the synthesis of such carriers is difficult, the use of less toxic natural molecules, such as sterols is a good alternative.The biliary acids, in particular the cholic acid 1a (Fig. 1) and its methyl ester 1b can be particularly appropriate, because their structures present a rigid polycyclic core with three adjacent hydroxyl groups (Fig. 1) which can constitute a recognition site of sugars. Indeed, the results obtained previouslyshowed that methyl cholate 1b (Fig. 1) transports selectively the aldoses and their derivatives through the SLM [30,31].The selective transports of neutral or charged species through the biological membranes is essential for the cellular metabolism of the alive species. Moreover, the artificial membranes opened large prospects for applications in separation science. However, the thermodynamics and the mechanistic details of the membrane transport phenomena do not appear completely clarified.

Several models were proposed and theoretically treated in order to elucidate the processes of passive and facilitated transport.The theories which derive from these models are useful for the interpretation of systems of current transport and for the design of future systems even more selective and effective.For a facilitated transport through a SLM, three mechanisms are known:



Cholic acid, 1a, R = H



1b (3 D structure)
Methyl cholate, 1b, R = Me

Fig. 1. Structure of methyl cholate.

- A solution-diffusion mechanism (Fig. 2), where the carrier and the complex are mobile in the membrane and migrate in the opposite directions.
- A fixed-site jumping mechanism (Fig. 3), where the sugar moves while binding successively to several fixed carriers. fixed carrier is considered as a complexation site, such as it is the case in an ion-exchange membrane.The jumping mechanism, frequent in the PIM [32,33], is characterized by a percolation threshold, which corresponds to the minimal concentration of carrier required to have a measurable flux.The existence of a percola-

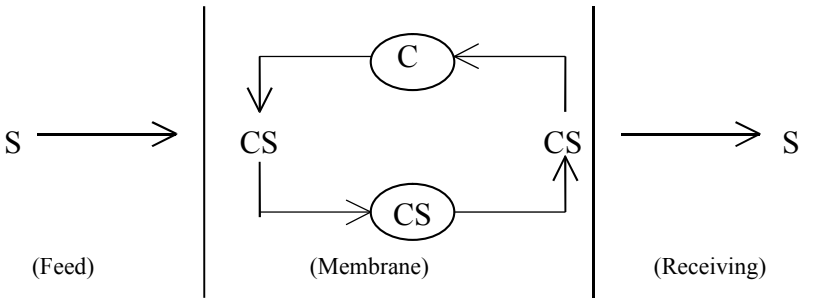


Fig. 2. Scheme of solution–diffusion mechanism.

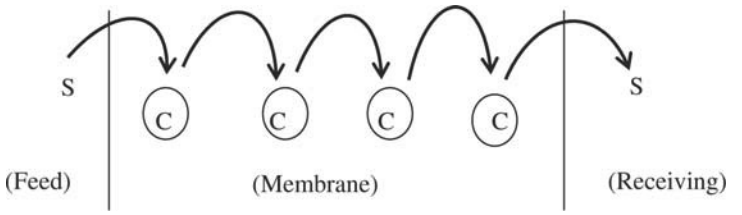


Fig. 3. Scheme of fixed-site jumping mechanism.

tion threshold is highlighted by studying the influence of the concentration of the carrier on the permeability of the membrane.

- A mobile-site jumping mechanism (Fig. 4), where the sugar moves while binding successively to several mobile carriers.This mechanism was proposed for the transport of sugars through a PIM, the carrier is a quaternary ammonium chloride which forms a pair of ions [33].

In this paper, we wish to report the carrier-mediated transport of various sugars through a supported liquid membrane system using the cyclohexane as solvent. The mechanism of transport was studied by determining the stability constant and apparent diffusion coefficient of carrier-sugar complex. The absence of a percolation threshold excludes a fixed-site jumping mechanism. An inverse proportionality between the stability constant and the apparent diffusion coefficient suggests a mobile-site jumping mechanism where the sugar is relayed along a sequence of mobile carriers.

2. Theoretical approach

The transport rate is measured by determining the increase of the sugar concentration c_R in the receiving phase versus time t. This rate is related to the flux J of sugar by Eq. (1):

$$\frac{dc_R}{dt} = \frac{J \cdot S}{V} \tag{1}$$

where S is the membrane area and V is the volume of the receiving phase.

When the system reaches a quasi-steady state, the flux J is related to Δc, the difference between the concentrations of sugar in the feed phase (c_F) and the receiving phase (c_R), and the membrane thickness l by Eq. (2) derived from Fick's first law:

$$J = \frac{P \cdot \Delta c}{l} \tag{2}$$

where P is the permeability of sugar through the SLM.

Since the flux of sugar is very large, the concentration (c_R) of the receiving phase is not negligible versus the concentration (c_F) of the feed phase. Thus, Δc is calculated using Eq. (3) where c_0 is the initial concentration of sugar in the feed phase:

$$c_F = c_0 - c_R \quad \text{and} \quad \Delta c = c_0 - 2c_R \tag{3}$$

Combining Eqs. (1), (2) and (3) yields differential Eq. (4):

$$P\,dt = \frac{(l\,V/S)\,dc_R}{c_0 - 2c_R} \tag{4}$$

Integration of both terms of Eq. (4) yields Eq. (5):

$$P(t - t_L) = \frac{l \cdot V}{S}\frac{1}{2}\ln\frac{c_0}{c_0 - 2c_R} \tag{5}$$

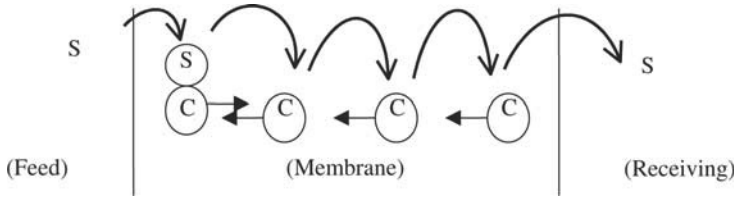


Fig. 4. Scheme of mobile-site jumping mechanism.

which shows that after an induction period (t_L) that may last up to several hours, the term –ln (c_0 – $2c_R$) is a linear function of t. The permeability P values for the various sugars were calculated, using Eq. (6), from the slopes a of the plots.

$$P = \frac{a \cdot V \cdot l}{2S} \tag{6}$$

The intersection of the linear section with the time axis defines the "true initial time" t_L at which the sugar concentrations in the aqueous phase are $c_F \approx c_0$ and $c_R \approx 0$. At this instant, the initial value of the flux, J_i, can be calculated by Eq. (7) derived from Eq. (2):

$$J_i = \frac{P \cdot c_0}{l} \tag{7}$$

The carrier-mediated mechanism for the transport of sugar is based on the rapid formation of a complex between the carrier (C) and the sugar (S) at the membrane-feed phase interface. This complex diffuses in the SLM in the rate-determining step and is eventually dissociated at the membrane-receiving phase interface. Such a mechanism is classically associated with a saturation kinetic law with respect to the sugar concentration.

The initial flux of sugar J_i is obtained by Eq. (7).

The experimental rate law shows, for the initial flux J_i of sugar, a linear dependence on $[C]_0$, the concentration of carrier in the membrane. Eq. (8) is a saturation law with c_0, the initial concentration of sugar in the feed phase:

$$J_i = \frac{\left(D^*/l\right)[C]_0 Kc_0}{1 + Kc_0} \tag{8}$$

where l is the membrane thickness. D^* is the apparent diffusion coefficient of the complex, and K is the stability constant for the interfacial equilibrium:

$$C(org) + S(aq) \rightleftarrows CS(org)$$

where (org) and (aq) refer to the organic and aqueous phase, respectively.

A linear plot, Eq. (9), can be obtained from Eq. (8) by the Lineweaver-Burk method:

$$\frac{1}{J_i} = \frac{l}{D^*[C]_0 K}\frac{1}{c_0} + \frac{l}{D^*[C]_0} \tag{9}$$

Such plots were drawn for various sugars, by performing a series of transport experiments with c_0 varying in the 0.40–0.025 M range. For each sugar, the values of the complexation parameters K and D^* are calculated from the slope and intercept of the plot obtained by linear regression:

$$K = \frac{\text{intercept}}{\text{slope}} \quad \text{and} \quad D^* = \frac{1}{[C]_0}.$$

3. Experimental

The sugars and other chemicals were commercial products (Aldrich) of the purest available grade, used as received. Methyl cholate was purchased from ICN Biomedicals and used as obtained.

The SLM support was a flat sheet of microporous poly(vinylidene difluoride) film Millipore HVHP of thickness 96 μm. Characteristic values are porosity 60% and pore diameter 0.45 μm. The membrane area available for diffusion was 19.6 cm^2 (diameter 9.0 cm). The support was first impregnated with a solution of methyl cholate in acetone and evaporated to dryness. The mass of methyl cholate present in the SLM was determined by calculating the difference between the initial mass of the support and its mass after impregnation and complete drying of the acetone used to dissolve the carrier. Before use, the SLM was conditioned in pure water.

The transport cell (Fig. 5) is made of two compartments of equal volumes (130 mL) separated

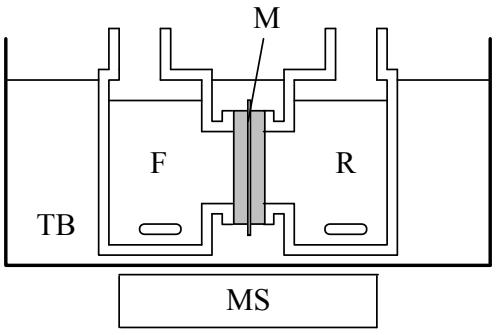


Fig. 5. Scheme of the transport cell. M is the SLM. F is the feed phase. R is the receiving phase. TB is the thermostated bath. MS is the multiple stirrer. Phases F and R are stirred using magnetic bars.

by the SLM. The cell is immersed into a thermostated bath (T = 25°C). The solutions in both compartments are stirred with magnetic bars at a constant rate.

The samples were analyzed using a HPLC apparatus equipped with a 30 cm Phenomenex Rezex column in calcium form, maintained in an oven at 85°C. The eluent was pure water, degassed and filtred with a cellulose ester membrane (Millipore, pore diameter 0.45 μm). The flow rate was 0.6 mL/min. The pump was a Shimadzu LC-9A model. Detection was achieved with a Varian RI-4 refractometer. Data acquisition was performed with the Varian Star software.

4. Results and discussion

4.1. Relation between the sugars structure and the complexes stability

The relation between the stability constants K and the structure of sugars was specified by considering a molecular model of the methyl cholate and by representing its interaction with various sugars. The determination of the crystalline structure of the cesium cholate [34] proved that the sterol core is almost plane, with three parallels hydroxyl groups (H0-3,7,12) pointing in the same face (Fig. 1). We estimated the distances between these hydroxyl groups by using the Viewer ACD/3D software [35]:

O3-O7 = 480 pm, O12-O7 = 450 pm,

O12-O3 = 700 pm.

The distance between O-3 and O-12 is longest.

If we suppose that the interaction between sugar and carrier is more intense when the hydroxyl groups of sugar are located close to those of the HO-3,7,12 system of the methyl cholate, sugars in which the three hydroxyl groups have a geometry close to that of the triol group of the carrier must be preferentially complexed with the carrier.

The distances between the hydroxyl groups of sugars were determined with the same software as for the methyl cholate. The average distance between two adjacent equatorial hydroxyl groups is 285 pm. The distance between two hydroxyl groups in the β form such as HO-2,4 is 420–480 pm, according to the axial or equatorial orientation of the groups. A particularly favourable situation is that of sugars having hydroxyl groups separated by a distance from 700 pm, which allows an ideal interaction with the HO-3,12 groups of the carrier. It is the case of sugars which have a HO-6 exocyclic group. By considering that the HO-6 group can freely turn around the C-5,6 bond, the distance between HO-2 and HO-6 is from 450 to 650 pm. Thus, the sugars which have a HO-6 group can engage a triol system with a HO-2 group which can bind closely with the triol system of the carrier.

For the sugars which do not have a HO-6 group, the longest distance is 550 pm between HO-1,4. This distance is lower than 700 pm, which can explain low stabilities of the complexes of the methyl cholate with the 6-deoxysugars compared to those of corresponding hexoses.

4.2. Relation between the stability constant and the apparent diffusion coefficient

Table 1 shows the results obtained for the sta-

Table 1
Relation between the stability constants K and the apparent diffusion coefficients D^* of the complexes carrier-sugar

Sugar	K ($mol^{-1}.L$)	$10^6 D^*$ ($cm^2.s^{-1}$)	$1/K$ ($mol.L^{-1}$)	$10^6 K.D^*$ ($mol^{-1}.L.cm^2.s^{-1}$)
Glucose	2.13	6.51	0.47	13.87
Galactose	2.51	5.49	0.40	13.78
Mannose	2.26	5.60	0.44	12.66
Xylose	1.07	15.50	0.93	16.59
Ribose	1.02	16.51	0.98	16.84
Arabinose	0.96	18.59	1.04	17.85
Fructose	2.17	6.06	0.46	13.15
Glucitol	1.77	6.26	0.56	11.08
Xylitol	0.89	19.92	1.12	17.73
Ribitol	0.85	20.64	1.18	17.54
Methylglucopyranoside	2.29	6.97	0.44	15.96
Methylgalactopyranoside	1.55	10.21	0.65	15.83
Methylmannopyranoside	1.29	10.74	0.78	13.85
Methylxylopyranoside	0.79	17.72	1.27	14.00
2-deoxyglucose	1.65	11.33	0.61	18.69
2-deoxygalactose	1.73	8.85	0.58	15.31
3-*O*-methylglucose	1.38	12.22	0.72	16.86
Fucose (6-deoxygalactose)	1.37	12.28	0.73	16.82
Rhamnose (6-deoxymannose)	1.14	12.62	0.88	14.39

K is the stability constant and D^* is the apparent diffusion coefficient

bility constant K and the apparent diffusion coefficient D^* of different studied complexes.

The values of K are always low (from 0.79 to 2.51). This point is in agreement with the theory which indicates that an effective transport requires a complex not very stable, which can be formed in the upstream interface and dissociated in the downstream interface of the SLM [36].

The values of D^* are always abnormally large. Indeed, we know that for simple sugars in aqueous solutions, the values of D^* are about 5×10^{-6} ($cm^2.s^{-1}$) ([37], examples: 6.7×10^{-6} ($cm^2.s^{-1}$) for glucose and 4.5×10^{-6} ($cm^2.s^{-1}$) for sucrose).

A solution-diffusion mechanism, in which the rate-determining step is the diffusion of CS complex in the SLM, cannot justify all the experimental results. It is necessary to more finely analyze our results to propose a concordant mechanism with these results.

If we compare the apparent diffusion coefficient D^* and the stability constant K of the various complexes, we observe that the stability constants vary in opposite direction of the apparent diffusion coefficients.

To check if there was a relation of opposite proportionality: D^* = constant/K or $K.D^*$ = constant, we used two methods. Initially, the product $K.D^*$ was numerically calculated for all studied sugars. Table 1 shows that the value of this product is approximately constant, $(15.4 \pm 4)\ 10^{-6}$ ($cm^2.s^{-1}.L.mol^{-1}$), for a series of sugars of different sizes and configurations. Then, to represent graphically this relation, we traced the apparent diffusion coefficient D^* versus the reverse of the stability constant $1/K$ of the complexes (Fig. 6). We observed that the graph of D^* vs. $1/K$ forms a group of dots distributed around an average line whose equation is: $D^* = 17.91\times10^{-6}/K - 1.63\times10^{-6}$.

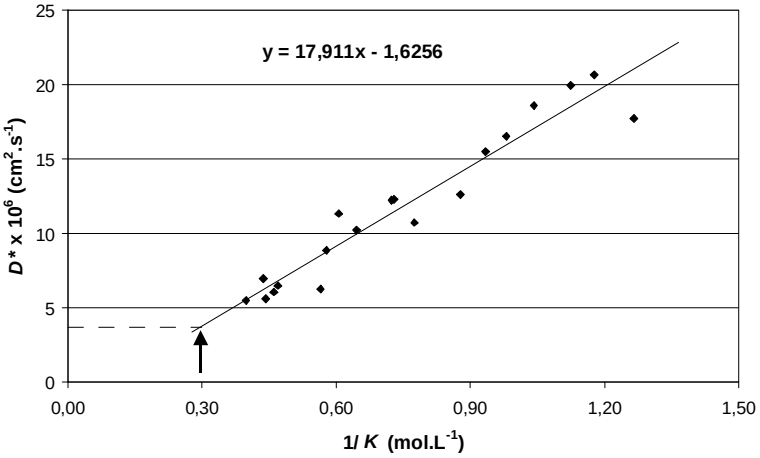


Fig. 6. Variations of the apparent diffusion coefficients D^* vs. the reverse of the stability constants K of the complexes of the methyl cholate with aldoses, alditols, deoxysugars and the methylpyranosides.

4.3. Mechanism of transport

The product $K.D^*$ = constant implicates that the complexes which migrate quickly are unstable, which is not a classical result. Indeed, in a solution-diffusion mechanism, the permeability must depend essentially on the value of the stability constant K, because all complexes have similar values of D^* (since the sizes of complexes are comparable). The relation observed between D^* and K is thus unexpected and requires an interpretation.

Obtaining a negative ordinate at the origin for the plot of Fig. 6 is surprising, but may be due to the poor accuracy on the intercept value. It is obvious that D^* does not become negative for very stable complexes ($1/K$ low). The results can be rationalized as follows:

1. When K is small ($1/K$ large, complexes very unstable), the apparent diffusion coefficient D^* is inversely proportional to K. It is the oblique part of the graph of Fig. 6. To interpret this result, a mechanism is proposed below.
2. When K is large ($1/K$ small, complexes very stable), the classical solution-diffusion mechanism occurs, where the species which migrates in the rate-determining step is the CS complex. We estimated D^* of CS by comparison with the values known for some sugars: 6.7×10^{-6} ($cm^2.s^{-1}$) for glucose (M = 180 g/mol) and $4.5\ 10^{-6}$ ($cm^2.s^{-1}$) for sucrose (M = 342 g/mol) [37]. For this aim, we used the Stokes–Einstein equation that states that the diffusion coefficient of spherical molecules is inversely proportional to the cubic root of their mass. Knowing the molar mass of the carrier (M = 422 g/mol), we calculate (without taking account of water) that a CS complex of monosaccharide has a mass close to 600 g/mol. If we take an average value of $D^* = 6\times10^{-6}$ ($cm^2.s^{-1}$) for a monosaccharide, we find that D^* is close to 4.2×10^{-6} ($cm^2.s^{-1}$) for CS. We did not try to specify more this value, since D^* also depends on the shape of the molecule which diffuses.

In Fig. 6, we traced the horizontal corresponding to this value of D^* for the small values of $1/K$, close to the origin. The intersection between this horizontal and the oblique segment define by its abscissas the minimum value of stability constant of a CS complex which migrates by simple diffusion. In Fig. 6, we found that this intersec-

tion is at $1/K = 0.30$ which corresponds to $K = 3.3$ approximatively. This value is only estimated, because we did not find sugars for which $K >$ 2.51 L/mol during this study.

For less stable complexes ($1/K > 0.30$), it is the other mechanism which governs transport. In the oblique part of Fig. 6, where K is small ($1/K$ large, complexes very unstable), we note that D^* become large, much larger than those determined for the diffusion of sugars alone [37]. Such values cannot be explained by the solution-diffusion mechanism.

Therefore, it is necessary to imagine a mechanism allowing a faster transport. A fixed-site jumping mechanism is excluded, since we do not observe a percolation threshold [30,31]. But the experimental results for unstable complexes can be explained by a mobile-site jumping mechanism [33]. Indeed, this mechanism requires that the complex is not very stable so that it dissociates easily and quickly to allow the sugar to jump from a carrier to the other one. On the other hand, the jumps of sugar between a CS complex and a carrier C are necessarily directed in the direction favorable for transport. This orientation of the jumps between mobile sites must allow a faster transport than the simple diffusion. Indeed, the simple diffusion due to the Brownian movement is made in all directions and goes in the direction of transport only at the macroscopic level, by a statistical effect. It is for this reason that a directed diffusion must be faster than the simple diffusion.

This idea is based on an analogy with the Grotthus mechanism [38,39] invoked to explain the quick diffusion of the proton in aqueous solution. Let us recall that the proton migrates more quickly than permitted by a law of simple diffusion. It is admitted in this case that during a shock between a solvated proton symbolized by H_3O^+ and a molecule of water, a proton is captured by the molecule of water which becomes a new ion H_3O^+ while the former ion H_3O^+ became a molecule of water. The proton does not move physically, but "jumps" from a water molecule to another one. In reality, it is the electronic doublets which "jump" and not the proton, but this mechanism causes a progression of the proton in space.

The scheme of Fig. 7 shows how the proton is apparently moved towards the right by a simple rocking movement of the doublets, without any movement of atoms in the solution. The movement of the proton between two water molecules is compared with that of sugar between two molecules of carrier (Fig. 4). Let us recall that, just as the proton cannot exist alone in water without being combined with a water molecule, sugar molecules cannot exist alone in the organic solvent where their are not soluble and must be associated with a carrier molecule.

The mobile-site jumping mechanism that we suggest is apparently that proposed by White [33] to interpret the mechanism of transport of sugars in the case of a PIM (polymer inclusion membrane). However, the criteria retained by White are different from those which we propose, and in our opinion, are not convincing. First, White observed a percolation threshold, classical result for the PIM in which the carriers are immobilized. However, if the sites are mobile, the existence of this percolation threshold becomes surprising. Conscious of this contradiction, White argued that the carriers in the PIM were immobilized, but "locally mobile". The other argument of White relates to the reduction in the permeability when

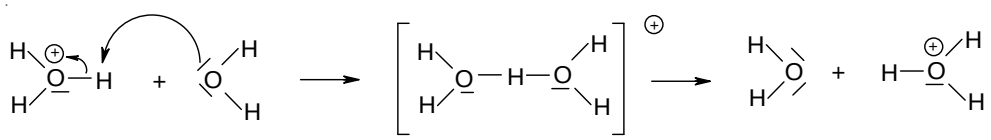


Fig. 7. Scheme of the transport of the proton in water.

the size of sugar or the carrier increases, whereas a mechanism by simple diffusion would lead to the same observations.

On the contrary, for the SLM described in this work, the intervention of a mobile-site jumping mechanism is based on the graph of Fig. 6, which shows the increase of D^* vs. $1/K$. This original phenomenon, which was never described to our knowledge, can be explained, in our opinion, only by a mobile-site jumping mechanism. The existence of an opposite correlation between D^* and K could even constitute an essential criterion to characterize this type of mechanism in other systems.

5. Conclusion

The determination of stability constants K allows to specify the nature of the complexes formed between the methyl cholate and several sugars. The values of the apparent diffusion coefficient D^* and of the stability constant K of the carrier-sugar complexes present notable differences, which confirms the molecular recognition of sugars by the methyl cholate. The presence of the $HOCH_2$ group is necessary to form stable complexes with the methyl cholate, which can be related to the long distance between O-3 and O-12 of the methyl cholate.

The dependence of the initial flux with the concentration of sugar and that of carrier shows that the rate-determining step in the mechanism of transport is the diffusion of the carrier–sugar complex through the SLM. However, the inverse proportionality between the complexation parameters K and D^* suggests, in the case of the unstable carrier-sugar complexes, a mobile-site jumping mechanism. The directed diffusion obtained when the sugar is relayed along a sequence of carrier can explain the large values observed for D^*, compared to a simple diffusion.

Symbols

- a — Slope of the plot $-\ln (c_0 - 2c_R) = f(t)$
- c_0 — Initial concentration of sugar in the feed phase, $mol.L^{-1}$
- c_R — Concentration of sugar in the receiving phase, $mol.L^{-1}$
- D^* — Apparent diffusion coefficient of the complex CS, $cm^2.s^{-1}$
- J_i — Initial flux of sugar, $mmol.cm^{-2}.s^{-1}$
- K — Stability constant of the complex CS
- l — Membrane thickness, mm or **µ**m
- P — Permeability of sugar, $cm^2.s^{-1}$
- S — Membrane area, cm^2
- $[C]_0$ — Concentration of carrier in the membrane, $mol.L^{-1}$
- $[CS]$ — Concentration of the complex CS, $mol.L^{-1}$
- T — Temperature, K or °C
- t — Time, s
- V — Volume of the receiving compartment, cm^3

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